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Dissociative Recombination: Theory, Experiment and Applications

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FOREWORD

The International Conference on Dissociative Recombination: Theory, Experiment and Applications was held at Chateau Lake Louise, Alberta, Canada from May 28-31, 1988. This symposium brought together many leading investigators in the fields of molecular ion recombination research, interstellar chemistry, aeronomy, plasma physics, and atomic and molecular theory and experiment. Participants presented talks reviewing their work and these were followed by lively discussion sessions. The papers in this volume are based on these talks with the exception of contributions from H. Nakamura and H. Michels, who were unable to attend. A list of attendees is given at the end of this volume.

We would like to express our gratitude to the United States Air Force Office of Scientific Research and to the National Aeronautics and Space Administration for financial support which contributed greatly to the success of the meeting. Thanks are due to the Centre for Interdisciplinary Studies in Chemical Physics at the University of Western Ontario and to the Institute for Scientific Research for providing administrative assistance. Special mention must also be given to C. Bottcher, A. Giusti-Suzor, T. Morgan, J. Peterson, D. Smith and W. Stwalley for chairing the sessions.

August, 1988

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INTRODUCTION TO DISSOCIATIVE RECOMBINATION

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Dissociative recombination (DR) of molecular ions with electrons has important consequences in many areas of physical science. Even though almost 40 years have elapsed since the first experimental and theoretical investigations of DR, it continues to present great challenges to the investigator.

For the diatomic or polyatomic molecular ion AB^+, DR is described by

$$AB^+ + e^- \rightarrow A + B$$

where e^- is an electron and A and B are atoms or molecules that may be in their ground states or vibrationally and/or electronically excited.

The last decade has seen something of a revolution in the study of DR, since ab initio calculations coupled with resonant scattering theory and multichannel quantum defect studies have produced detailed results illuminating the role of ion vibrational excitation, the quantum yields of the DR products, and the role of Rydberg states. The old assumption that for most molecules the DR rate coefficient is about 10^{-7} cm^3/sec is clearly no longer adequate. Indeed, it is now clear that the simplest ions, e.g. H_2^+ and He_2^+, have considerably slower total

DR rate coefficients from their ground vibrational levels. H_3^+, the most important ion in hydrogen plasmas, has been shown theoretically and experimentally to recombine much more slowly when vibrationally cold than once believed. Deep narrow resonances associated with Rydberg state interactions have been predicted and observed. New decay channels have been found and the effects of vibrational excitation are being clarified as theorists probe the details and experimentalists obtain better control of their experiments.

I. Theory

The early experimental results of Biondi and Brown[1] and Holt et al.[2] on rare gas afterglows coupled with the need to explain the electron concentrations in the earth's ionosphere[3] led Sir David Bates to first propose a mechanism for DR in 1950[4] in a seminal paper that was less than one full page in length. The mechanism has stood the test of time and is still the basic mechanism used to describe DR in the absence of the higher order role due to Rydberg states. The proposed mechanism was several years in the making because it had to overcome two important obstacles. First, due to the mass mismatch, a collision with an electron could not be expected to cause a massive molecule to fall apart. The transfer of electronic energy to the nuclear motion is improbable. However, in Bates's proposed mechanism, the electron energy is transferred entirely to the electrons of the target molecule and a neutral state is formed in which the nuclear motion leads to the dissociation of the molecule. The process is illustrated in Figure 1 where a molecular ion, AB^+, shown by the solid potential curve captures an electron of energy ε into repulsive state AB. Once the interparticle distance between A and B becomes sufficiently large, the electron can no longer be ejected and the process is said to be stabilized. The second obstacle, as pointed out in the paper in this volume by O'Malley, is the non-crossing rule which requires that curves of the same molecular symmetry do not cross. According to this rule, the repulsive state labelled AB in Figure 1 could not reach the ion

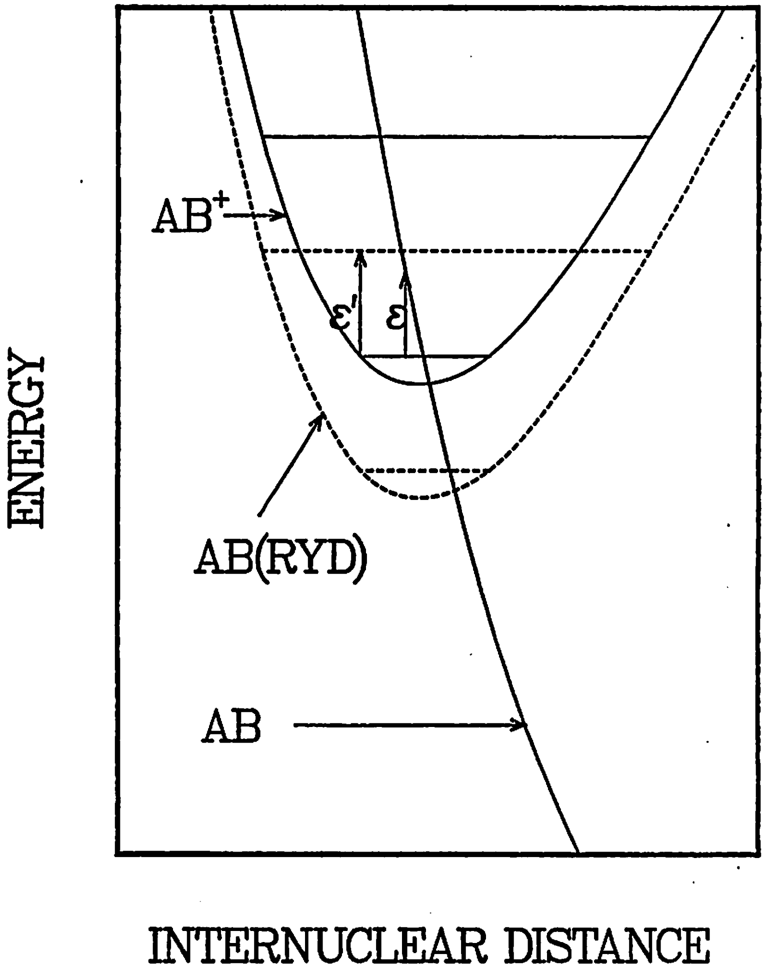

Fig. 1. Dissociative Recombination Mechanisms

because it would have to cross through an infinite number of Rydberg states of the same symmetry as AB and having the ground state of the ion as a series limit. It is now understood however, that the repulsive state, AB, is a diabatic state, i.e., it is not an adiabatic solution of the full Schroedinger equation and therefore does not violate the non-crossing rule.

The first detailed calculations of DR were done by Bardsley[5] who used the configuration mixing (CM) or resonant scattering theory approach. Bardsley also introduced Rydberg states into DR via indirect recombination.[6] In this process, the electron is captured directly into a vibrationally excited Rydberg state by Born-Oppenheimer breakdown (vibronic coupling). In Figure 1, this process is illustrated for an electron of energy ε'. The Rydberg state is then predissociated by the neutral AB repulsive state.

A recent important development is the application of multichannel quantum defect theory (MQDT) to DR by Lee[7] and Giusti-Suzor.[8] In the first article in this volume Giusti-Suzor reviews the main features of both the CM and MQDT approaches and describes the role played by vibrationally excited Rydberg states which appear as resonances in the DR cross sections. These Rydberg states participate in DR by both a non-Born-Oppenheimer coupling described above and by an electronic coupling. For the non-Born-Oppenheimer coupling, the largest matrix elements involve a change of unity in the vibrational quantum number. In practice, this can usually be satisfied by high principal quantum numbers near about seven. On the other hand, the electronic coupling between the Rydberg and dissociative valence states is largest for the lowest Rydberg state and decreases approximately as $n^{*-3/2}$ where n^* is the effective Rydberg principal quantum number. In this mechanism, Rydberg states with low principal quantum numbers but considerable vibrational excitation can play a role. This electronic coupling mechanism has been the subject of important studies by O'Malley[9] and Hickman,[10] and Hickman[10] has shown that the electronic coupling can be considerably larger than the vibronic coupling.

In the second paper in this volume, O'Malley reviews the use of the resonant scattering theory approach to DR with the assumption that the various processes that drive DR are localized in the internuclear distance coordinate. This approximation is especially applicable if the dissociative state does not have a steep slope. O'Malley finds that the electronic coupling mechanism leads to the surprising result that the cross section for the case of a single isolated resonance has a dip at the energy of the Rydberg state vibrational level.

The electronic coupling mechanism between the Rydberg and dissociative states is explored in the paper by Hickman. He shows that the capture is given by a matrix element of a Green function and is second order in the electronic coupling between the electron-ion and dissociative states. These higher order couplings are present in the second and higher terms on the right side of Eq. (5) in the paper by Giusti-Suzor. Hickman also compares the CM and MQDT approaches and points out that for the case of a single isolated resonance, the resonant scattering theory approach in the Independent Resonance Approximation[10] and the MQDT approach lead to the same expression for the DR cross section. The expression takes the form of a Beutler-Fano profile with a non-zero q. A study of DR in H_2^+ shows that the net effect of the indirect process depends upon whether the direct process is fast or slow.

Large scale ab initio results for DR potential curves for O_2 and N_2, and electron capture widths and DR rate coefficients for O_2 are reported in the paper by Guberman. He finds that for O_2, out of the 11 states that can produce $O(^1S)$, the upper state of the green line, only a single state is important for the lowest 9 vibrational levels of the ion. The DR rate coefficient is very sensitive to vibrational excitation. The maximum rate coefficient for generating $O(^1S)$ is from v=2 and is 78 times greater than the rate coefficient from v=0. For $O(^1D)$, three states are important for generating the upper state of the red line from the lowest three vibrational levels of the ion. The $O(^1D)$ rate coefficients are less sensitive to vibrational excitation than the $O(^1S)$ rate coefficients with the rate coefficient from v=2 being a factor of 2 less than the rate coefficient from v=0. The calculated $O(^1D)$ rate coefficients are in good agreement with rate coefficients deduced from satellite measurements. For N_2, DR from v=0 is dominated by four states and an inspection of the dominant configurations indicates that the $^3\Pi_u$ states may have the highest rate coefficients.

Large scale CASSCF calculations are reported by Kraemer and Hazi on the potential curves which describe the DR of HCO^+. Their approach leads to rather accurate values for electronic excitation energies in CO and HCO and an accurate dissociation energy for HCO^+. Since a favorable recombination rate coefficient would require a similar geometry for the linear ion and the neutral state containing the captured electron, they hold the CO internuclear distance at the separation found in HCO^+ while varying the CH distance. In a linear geometry, none of the neutral states give likely dissociative routes from the lowest vibrational level of the ion. While two of the potentials drop significantly after relaxing the CO separation, a favorable dissociative route is still not found in spite of the fact that the laboratory DR rate coefficients are high. They suggest several possible indirect mechanisms.

Nakamura, Takagi, and Nakashima report results for the DR of H_2^+ (and isotopes) and CH^+. For H_2^+, an interesting isotope effect is reported from the v=3 vibrational level of D_2^+. At about 0.5 eV electron energy, the cross section for D_2^+ is very small compared to the cross sections for H_2^+ and HD^+. The shape of the window resembles the DR Franck-Condon type windows found in model calculations.[11] For vibrational excitation from the v=1 state of HD^+, they show that the energy dependence of the cross section is similar to that for DR indicating that the repulsive states are the intermediate states. Above the threshold energy, the v=1 to 2 vibrational excitation cross section is of comparable magnitude to the DR cross section. For CH^+, they find that the DR rate coefficient is about 1 x 10^{-7} cm^3/sec at T=120K in agreement with the result of the merged beam experiment.[12]

Associative ionization (AI), is related to DR by detailed balance and many of the same theoretical techniques developed for DR can be used for AI. Urbain describes some recent MQDT calculations on AI in H_2 and several recent experimental developments. For the case where the separated atoms limit lies below the lowest vibrational level of the ion, the AI cross section increases with energy above threshold as new vibrational channels become accessible. Above the ion asymptote, Penning ionization competes and the AI cross section decreases. For the case of H^+ colliding with H^-, the entrance channel asymptote is above the lowest vibrational level of the ion and the cross section is large at zero energy decreasing inversely with the increasing energy. Experiments are described which provide for a measurement of the AI cross section by detection of either the emitted electron energy spectrum or of the vibrationally excited product ion. The generation of H(2s) and H(3s) atoms for AI experiments is described.

Since the neutral excited states of HeH lying beneath the ground state of HeH^+ all have the attractive ion core, there are no excited repulsive states which can lead to DR of the ion ground state. The paper by Michels describes the calculation of dissociative routes which can potentially lead to DR of excited states of HeH^+. The lowest ion excited state is only weakly bound and the calculated series of quartet states do not appear to offer favorable routes for DR. An additional doublet series is difficult to calculate since it can autoionize to the ion ground state. A second quartet Rydberg series which can provide DR routes for three higher excited states of the ion but which can also autoionize to a lower ion state is also discussed.

II. Experiment

The merged beam technique is described in the paper of Mitchell and Youssif. Recent measurements of the total DR cross sections for H_2^+, H_3^+, HeH^+, and N_2^+ and of the branching ratio for H_3^+ recombination are discussed. A new channel leading to H_3^* has been identified in the latter measurement. HeH^+ has been measured to have a nonnegligible recombination cross section, although the state of excitation of the ions used in the experiment has yet to be determined. Deep resonant structures have been observed in the cross sections of H_2^+, HeH^+ and N_2^+.

Adams and Smith have brought the Flowing Afterglow Langmuir Probe (FALP) technique to the forefront of recombination research in recent years. An important advantage of this technique is the fact that ion formation and decay occur in different regions of the flow apparatus and so the ions have time to relax internally before their recombination rate is studied. Measurements of H_3^+ recombination with this technique have shown that the rate coefficient for de-excited ions is less than $10^{-8}cm^3/sec$. This has been confirmed by recent merged beam experiments. (See Mitchell and Yousif, this volume). Subsequent studies have found that measured values for He^+,HeH^+ and H_3^+ rate coefficients are indistinguishable. In a plasma, collisional radiative recombination (CRR) must be considered. In the FALP method where electron densities of $10^{10}cm^{-3}$ are encountered, CRR can proceed with a rate coefficient of about $10^{-9}cm^3/sec$, thus setting a lower limit to the measurable dissociative recombination rate coefficient. CRR may also have contributed to recently measured high values of H_3^+ recombination published by Amano.[13] The FALP technique has been extended to the determination of recombination rate coefficients for a wide variety of protonated species and efforts are underway to introduce UV absorption spectroscopy and laser induced fluorescence techniques to measure branching ratios for DR.

Earlier experiments performed using the microwave afterglow technique have been re-examined by Johnsen. It has been found that (a) the presence of molecular additives in a plasma leads to a lowering of the mean electron temperature, and (b) heat conduction in a plasma is insufficient to produce a uniform electron energy distribution over the whole volume. The consequence of these findings is that some of the earlier values for measured recombination rate coefficients must be treated with suspicion. This is particularly true for cluster ions. A reassessment of previous N_2^+ studies is given in the light of recent research on the vibrational deactivation of diatomic ions. Although it is concluded that previous studies applied to vibrationally excited ions, skepticism is expressed concerning the new merged beam results discussed by Mitchell and Yousif. Mention of new studies concerning electron-ion recombination at elevated gas densities and of recent ion-ion recombination work is also given.

Spectroscopic measurements of the product state branching ratios following the DR of N_2^+, O_2^+, CO_2^+, and H_2O^+ in a flowing afterglow, as a function of the initial vibrational excitation of the parent ions, have been performed by Rowe and Queffelec. The H_2O^+ results support the conclusions of Herbst's statistical analysis of branching ratios rather than Bates' theory based on bond breaking.

Translational spectroscopy in which measurement of the kinetic energies of dissociation products allows a determination of their excitation state is a powerful tool which could be used for DR branching ratio measurements. The paper by van der Zande, Koot, Los, and Peterson provides an example of this elegant technique. A study of the energy spectra of the products of O_2^+ + Cs dissociative electron capture is presented. The high resolution inherent in the technique allows the Rydberg states into which the electron is captured to be identified.

A proposed experiment to demonstrate laser stimulated radiative recombination of electrons and protons is described by Morgan and Mitchell. The experiment will employ the Merged Beam Apparatus at the University of Western Ontario and will employ field ionization detection of the highly excited recombination products. The technique also has applications to the measurements of DR branching ratios and dielectronic recombination cross sections.

Recent theoretical and experimental studies by Lundeen on H_2 Rydberg states with high angular momenta have shown that the energies of these states may be accurately calculated using models employing long range interactions only. This is in contrast to the case for low l states where short range interactions dominate and MQDT theories are necessary for energy calculations. Furthermore, long range interaction theories predict short autoionization lifetimes (10^{-9}sec) for the high l states. Short range interaction theories, on the other hand, predict lifetimes of the order of tens of seconds. This implies that long range interactions play a crucial role in the dynamics of high l Rydberg states.

The paper by Graham addresses the subject of electron and ion temperatures in plasma discharges. A knowledge of these is important in order to determine the conditions under which DR acts as a major ion loss mechanism. Generally it is overshadowed by ion diffusion to the walls. DR, however, does play a major role in the production of excited atoms and so a knowledge of product branching ratios is important for the interpretation of plasma spectra which provide diagnostic information concerning the state of the discharge. DR also competes with dissociative attachment for low energy ions and so must be included in models of negative ion sources.

It is generally accepted that the primary formation mechanism for H^- ions in a pure hydrogen discharge is the dissociative attachment of electrons to vibrationally excited H_2 molecules. The source of this vibrational excitation is only partially understood. Hiskes and Karo have examined the role of wall collisions involving H_2^+ and H_3^+ in producing vibrationally excited hydrogen molecules. A description of the processes involved in the neutralization of these molecules at surfaces is given and the authors find that collisions of vibrationally excited H_2^+ and H_3^+ produce copious numbers of $H_2(v'')$ molecules. Indeed, this mechanism appears to be the dominant source of $H_2(v'')$ at low plasma densities.

Bahns and Stwalley provide a review of antimatter cluster ion formation principles. The impetus for this work is to produce antihydrogen in a condensed form for easy transportation and storage. The concept of the pseudowall, a cold, trapped, high density plasma within which many collision processes can occur leading to cluster ion buildup, is discussed. Experimental manifestations of the pseudowall are proposed.

Spectroscopy is an important tool in plasma diagnoses since it is generally non-perturbative. Interpretation, however, requires a good knowledge of the atomic processes leading to photon emission. Shoemaker, Ganguly, and Garscadden describe how a study of the Stark broadening of spectral lines from highly excited Rydberg states within the plasma can provide information on local electric fields. A description of the application of this technique is given.

III. Applications

DR can yield translationally hot products which may have energies that exceed those needed for planetary escape. The role of DR in the escape of N isotopes from Mars is discussed in the paper by Fox. Among several processes that contribute to planetary escape, DR of N_2^+ is the major process at high and average solar activities and is the most important process contributing to the isotope enhancement ratio. The isotope enhancement role of DR disappears for $v>0$. DR of O_2^+ is an important process in planetary atmospheres, where it generates $O(^1S)$ and $O(^1D)$, the upper states of the green and red lines, respectively. Fox discusses a detailed model of these emissions as a function of altitude in the nightside ionosphere of Venus. The model results for the green line emission are consistent with the measurements made by the Venera space probe.

Yee, Abreu, and Colwell discuss the modelling of the O(^{1}S) and O(^{1}D) emissions which result from DR of O_2^+ in the Earth's ionosphere. For the vibrational distribution of the ion they use five models developed by Fox. For the specific rate coefficients yielding ^{1}D and ^{1}S atoms, they use the values calculated by Guberman. In order to calculate yields for a distribution of vibrational levels, one must have a specific rate coefficient and a total rate coefficient for each level. Since total rate coefficients have not been measured or calculated for v>0, they use the laboratory v=0 coefficient for higher v. The adequacy of this assumption must await the results of future calculations or experiments. Their theoretical model shows that the ^{1}D (^{1}S) quantum yield decreases slightly (increases strongly) with vibrational excitation. A calculation of the quantum yields using the measured volume emission rates from the Atmosphere Explorer E satellite indicates that at high vibrational excitation, the calculated ^{1}S quantum yields are higher than the authors' theoretical model results but the ^{1}D results are in good agreement with the theoretical model.

The products of the DR of polyatomic molecules are important components of the chemistry of dense interstellar clouds. Herbst discusses three methods which have been used to determine these yields and comparative examples are given for H_3O^+, $HCNH^+$, and $C_4H_2^+$. The abundances of neutral complex molecules and of small molecules such as OH are sensitive to the model that is used. It is known that the ratio of singly deuterated species to their hydrogenic analogues is often higher than the deuterium to hydrogen ratio in the dense clouds. It is possible that the product branching ratios for DR reactions may account for this, but a definitive statement must await the independent determination of the DR branching ratios.

The role of DR in diffuse interstellar clouds is discussed by Black and van Dishoeck who point out that the concentrations of neutral species can be intimately affected by the products of DR reactions. They stress the need to determine the quantum yields of products resulting from DR of CH_3^+, $C_2H_2^+$, $C_3H_3^+$, and H_3O^+. In diffuse clouds, where the fractional ionization is high, the DR rate coefficient for H_3^+

significantly affects the column density of H_3^+, but in dense molecular clouds the column density is less sensitive to the DR rate coefficient. For HeH^+, the predicted model concentration is greater than the recently observed upper limit, indicating that an important sink is missing from the models.

Several approaches for determining the small ionization fraction in dense interstellar clouds based on deuterium fractionation are discussed by Turner. Reliable values of the DR rate coefficients of H_3^+ and CH_3^+ are needed for these models. The chemistry of cyanopolyynes is discussed and several possibilities are presented to account for the difference between the observed and model values for the ion to neutral concentration ratios. A model of the DR of $H_3C_2O^+$ is presented. Turner argues that the model supports the prediction of Bates for the likely quantum yields of the DR products.

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